

Self-assembled DNA networks and their electrical conductivity

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We report direct measurements of the intrinsic electrical characteristics of polynucleotides using a conducting-probe atomic-force microscope under vacuum. Poly(*dA*) poly(*dT*) self-assemble a cross-interlaced network on mica, but poly(*dG*) poly(*dC*) self-organize a uniform two-dimensional reticulated structure. Transport studies demonstrate that poly(*dG*) poly(*dC*) can act as a semiconducting nanowire and show a better conductance than that in poly(*dA*) poly(*dT*). © 2000 American Institute of Physics. [S0003-6951(00)01045-7]

DNA is an important and promising molecule, not only due to its genetic function, but also as a molecular scaffold for nanotechnology¹ and nanostructure.² DNA has the special double-helix structure with π -electron cores of well-stacking bases, which may be a good candidate³ for long-distance (e.g., 200 Å) and one-dimensional charge transport. These investigations have significant implications for the study of DNA damage and repair in biological systems,⁴ the application of DNA in electronic devices⁵ and DNA-based electrochemical biosensors.⁶ On the other hand, many research groups also show the divergent and controversial conclusions⁷ in DNA-mediated charge transport.

Recently, we found that polynucleotides with a specific base sequence self-assembled reticulation structure on mica. A drop (10 μ l) of DNA solution containing 250–125 ng/ μ l, was spread on the center of a freshly cleaved mica surface (1.5 \times 1.5 cm) and incubated for a minute, then the residue solution was blown off with a rubber ball and the sample was dried in a flowing N₂ gas. Figure 1 indicates the tapping-mode atomic-force microscope [(AFM) SEIKO Instruments] images of DNA network assembly at the concentration of 250 ng/ μ l. Poly(*dA*) poly(*dT*) [Fig. 1(a)] self-assemble a cross-linked network on mica. Various DNA chains cross over together and the 1.7 nm height of the junction is about twice the chain height of 0.8 nm. However, poly(*dG*) poly(*dC*) [Fig. 1(b)] self-organize a uniform reticulated structure with the same height of 2.1 nm between the junction and chain. The mesh size of the network is larger in poly(*dG*) poly(*dC*) than that in poly(*dA*) poly(*dT*). Formation of the network is strongly dependent on DNA concentration and substrate, which is easier on a hydrophilic surface (e.g., mica) than a hydrophobic surface (e.g., HOPG, gold). The lower the concentration, the larger the mesh size of network. When the concentration is less than 50 ng/ μ l, only the separated DNA fibers are observed.

For probing the electrical properties of the DNA molecule, a gold layer is evaporated by a Si(001) shadow mask contacted upon a DNA network to fabricate a conductive electrode [Figs. 1(c) and 1(d)]. A conducting probe⁸ AFM (JEOL Ltd.) [Fig. 2(a)] is performed to explore the local electrical characteristics of DNA bundles and single mol-

ecules. The sample is pretreated under vacuum (10⁻⁶ Torr) for 5–12 h. In order to protect the apex of the gold-coated tip and avoid the contaminated tip, noncontact mode is applied for imaging, then contact mode for probing $I(V)$ curves at an accurate position of the DNA chain. The point contact $I(V)$ measurement is controlled by the loading force. We found that the best loading force is located on 20–40 nN, forces over \sim 100 nN result in damage to the DNA, and force less than \sim 10 nN results in unreliable electrical contact. Furthermore, when we put the conducting tip on the position of mica without DNA near the edge of electrode, the detected current is on the noise level of \sim pA.

Figures 2(c) and 2(d) show the typical $I(V)$ curves of poly(*dG*) poly(*dC*). Two behaviors are observed: the linear Ohmic and *p*-type rectifying characters in varied measure position. In the case of poly(*dA*) poly(*dT*), the rectifying behavior is not observed and the linear $I(V)$ curves gradually tend to S-shaped $I(V)$ curves at the decreasing loading force

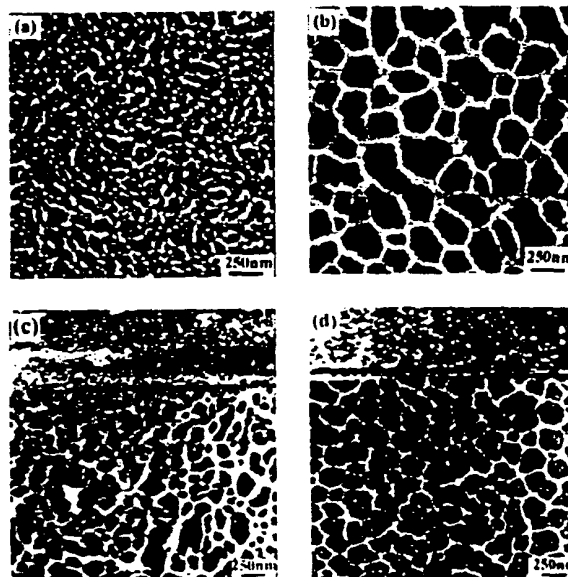


FIG. 1. Self-assembly DNA networks of (a) poly(*dA*) poly(*dT*)/5U and (b) poly(*dG*) poly(*dC*)/5U on mica. A gold electrode is evaporated on the DNA networks of (c) poly(*dA*) poly(*dT*)/4U and (d) poly(*dG*) poly(*dC*)/5U (1U = 50 ng/ μ l).

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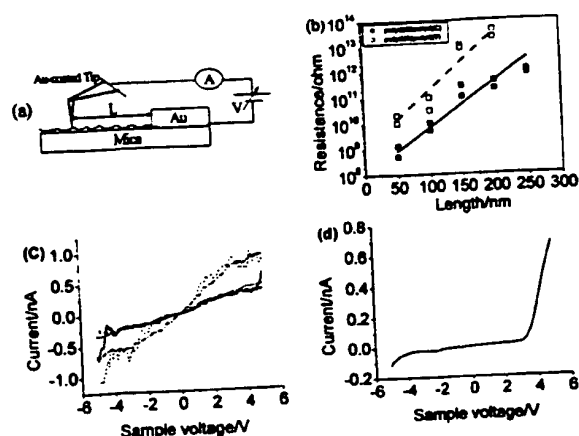


FIG. 2. (a) Schematic illustration of the measurement with the conducting-probe atomic-force microscope. (b) Relationship between resistance and DNA length. The exponential fitting plots of data are also shown. (c) Typical $I(V)$ curves of poly(*dG*) poly(*dC*), the linear Ohmic behaviors on $L = 100$ nm at the repeat measurement of five samples. (d) Rectifying curves of poly(*dG*) poly(*dC*) at $L = 100$ nm.

(and vice versa). At the area of high voltage, the $I(V)$ curves are unstable and fluctuate. We select the low-voltage (< 0.2 V) $I(V)$ values and get the relationship between resistance and DNA length. Figure 2(b) indicates that the resistance is exponentially dependent on the DNA length. Poly(*dG*) poly(*dC*) shows better conductance than poly(*dA*) poly(*dT*). By using the average resistance value of 50 nm, the resistivity of poly(*dG*) poly(*dC*) is estimated by $\sim 1 \Omega \text{ cm}$. That means poly(*dG*) poly(*dC*) can act as a conducting nanowire. We cannot get the $I(V)$ values at the tip-electrode distance less than ~ 40 nm, because the tip is directly contacted with the edge of the gold electrode and the current is very large.

Charge transfer and transport⁹ in DNA show an intriguing and complex behavior, depending on the different redox potentials¹⁰ of the bases, base-stacking characteristics, dynamic structural distortion of the DNA,¹¹ and energy constraint. Guanine (G) is the most easily oxidized and induced a hole carrier. Once charges (especially holes) are created on the uniform DNA chain, then the hopping charge transport can apparently occur among the discrete G sites or delocalized (e.g., polaron)³ GGG domains, and make poly(*dG*) poly(*dC*) a good hole conductor and *p*-type rectifying behavior.

The base-stacking characteristic is another important factor for charge transport in DNA. Two homopolymers poly(*dA*) and poly(*dT*) (270 mer, ~ 92 nm) are synthesized separately, then mixed and annealed to poly(*dA*) poly(*dT*) with an average length of 0.5–1.5 μm . The average length of poly(*dG*) poly(*dC*) is 5000–8600 base pairs (bps), i.e., 1.7–2.9 μm . The connection defect may exist between single chains in the DNA double helix, and lead to interchain tunneling or the superexchange process of charge transfer. As the DNA length increases, the defect also increases and results in the exponential dependence between resistance and

DNA length. Furthermore, the stacking distance of the adjacent base pairs also affects the π overlap. The crystal structure analysis¹² of oligonucleotides indicates that the axial rise of residue is 2.88 Å for poly(*dG*) poly(*dC*) and 3.22 Å for poly(*dA*) poly(*dT*). The more compact the structure of base stacking, the more favorable the charge transport. This results in better conductance of poly(*dG*) poly(*dC*) than that of poly(*dA*) poly(*dT*).

Finally, although the effects of water (H_2O) on the conductivity can be neglected under the vacuum treatment, the proton (H^+) and little Na^+ ions of the buffer solution (10 mM Tris-HCl, pH 7.6) remain on the DNA and mica surface, which might affect the π -stacking electric structure of DNA and the charge transport.

In summary, we have directly measured local electrical characteristics and distinct changes in the conductance of DNA networks, suggesting that poly(*dG*) poly(*dC*) is a promising semiconducting nanowire. By designing the specific DNA base sequence and controlling the connection junction of chains, it may be possible to the use of individual DNA molecules and networks as functional molecule electronic nanodevices.

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